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A NEW CONSTRUCTION OF HALOGEN-FREE FLAME RETARDANT INSULATED WIRE WITH DOUBLE LAYERS

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Summary

A few halogen-free materials with highly flame retardant properties have been so far reported for cable use, but none of them have been developed for insulated wires to attain UL Std.62 VW-1 Flame Test.

The authors were successful in developing a halogen-free insulated wire by using a combination of the newly developed halogen-free highly flame retardant material and double layers construction. The new construction consists of the outside layer of a highly flame retardant special ethylene-vi⁻⁻l acetate copolymer and the inside layer of c..mon polyolefin. These double layers are simultaneously extruded through the fixed die to cover a conductor and then crosslinked by an electron accelerator. This insulated wire, passing flame tests like IEEE-383 or UL Std.62 VW-1 and having excellent mechanical and electrical properties that satisfy LOCA Test requirements in IEEE-323, finds not only a particular application to nuclear power plants, but also other wide applications to appliance wires in general use because of the capability of continuous 40,000 hour service at 110°C and high oil resistance. In addition to the inherent halogen-free composition, surprisingly the observed CO generation was one-fifth that of natural polyethylene and no black smoke was produced in combustion.

1. Introduction

To protect peripheral equipment from corrosive gaseous HCl and prevent formation of black smoke and toxic gases during combustion of halogen compounds, a few halogen-free materials with highly flame re..ardant properties have so far[1) 2)] been studied for cable use in nuclear power plants, underground railways and ships. For internal wiring in appliances, however, halogen-free insulated wires that pass the flame test of UL Std.62 VW-1 have not been developed. Flame retardant XL-PVC or XL-FRPE insulated wires now in use produce halogen gases when the wires are used at high temperature for a long term, thereby corroding the periphery equipment. Amplifier relay circuits, which are liable to excessive temperature rise, pose an especially difficult problem.

To obviate such problems, halogen-free compounds can be used for insulation. These prevent the corrosion of equipment due to halogen compounds. However, if an attempt is made to achieve the VW-1 grade with ordinary polyolefine or polyolefine copolymer by using aluminum hydrates, it is necessary to impregnate aluminum hydrates of 2-3 times the polymer. The natural consequence is that the superior mechanical and electrical properties inherent to the polymer will be substantially reduced, thus making it unusable as an insulation material.

We have overcome this problem by developing wires of crosslinked double-layer insulation construction:
1) an outer layer of a newly-developed special ethylene-vinyl acetate copolymer (Special EVA) which is highly flame retardant and yet has a brittleness temperature as low as -20°C, and
2) an inner layer of common polyolefine with excellent mechanical, water-resistant and electrical properties.

Properties of Special EVA and test results of wires for appliance wiring and for general wiring of trial manufacture are presented in this paper.

2. Properties of Special EVA

2.1 Non-corrosive Special EVA

Non-corrosive Special EVA contains no halogen compounds. Consequently, it does not corrode metals.

The results of tests using the ASTM D2671 Corrosion Testing Method A are shown in Table 1. XL-PVC and XL-FRPE do corrode metals.

Table 1. Corrosive Property

(ASTM D2671)

Materials	OI	Condition	Result
XL-PVC*	29	180 C×17hr	Fail
XL-FRPE**	29	180 C×17hr	Fail
XL-EVA*** sper	48 min	180 C×17hr	Pass

* Crosslinked PVC
** Crosslinked flame Retardant PE
*** Crosslinked Special EVA

2.2 Smokelessness

The smoke optical density, C_S max., and the gases produced by combustion of various materials are shown in Table 2. Special EVA produces scarcely any smoke and transmits about 90% or more of light. Also, its CO generation is one-fifth that of flammable polyethylene.

Table 2. Smoke Optical Density and Gas Formation

Materials	OI	Smoke Optical Density (C_S max.)	Gas (mg/g)		
			HCl	CO	CO_2
XL-PVC	29	4.8	290	100	900
XL-FRPE	29	3.2	180	200	1200
XL-EVA spec.	48 min.	0.2	0	34	850
XL-PE****	18	0.02	0	170	1250

****None-flameretardant PE

Method:

- Determination of smoke optical density, C_S max., by JIS D1201 (1973). The concentrations of smoke produced by combustion of materials at the OI value of 0.5 higher than that of each material were obtained with the device shown in Fig. 1.

$$C_S \text{ max} = \left(\frac{2.3}{L}\right) \log_{10}\left(\frac{100}{T_{min}}\right)$$

where: C_S max = smoke optical density (maximum light reduction coefficient per 1m)
L = light path length, 0.5m
T_{min} = minimum transmission rate at the time of maximum smoke emission, %.

- Determination of gases produced by combustion.[3] A 0.5g specimen is placed in the heating oven shown in Fig. 2 and kept at 800°C for 30 min. Halogen is trapped by a sodium hydroxide solution. This is expressed as the amount of HCl according to the silver nitrate method described by JIS K0107 (1967). The other gases are analyzed separately by gas chromatography. The heating conditions are 800°C x 10 min.

$$S = 36.5 \times \frac{0.1 \cdot f(B-A) \cdot 1000/50}{W}$$

where: S = quantity of HCl produced, mg/g
A = consumption of 0.1N ammonium thiocyanate solution, mℓ
B = quantity of 0.1N ammonium thiocyanate solution consumed by a blank test, mℓ*

2.3 Mechanical, Electrical and Flame Retardant Properties

The mechanical, electrical and flame retardant properties of crosslinked Special EVA are shown in Table 3. The tensile strength is 0.6 kg/mm^2 - less than half that of PVC - however, it has excellent oil resistance and heat-aging properties. As a plastic offering such high flame-retardant properties as OI 48, UL 94V-0, by addition of aluminum hydrates, it retains excellent mechanical properties, such as a 550% elongation at ruptures and a brittleness temperature as low as -20°C.

Fig. 1 Oxygen Indexer and Smoke Optical Density Measuring Device

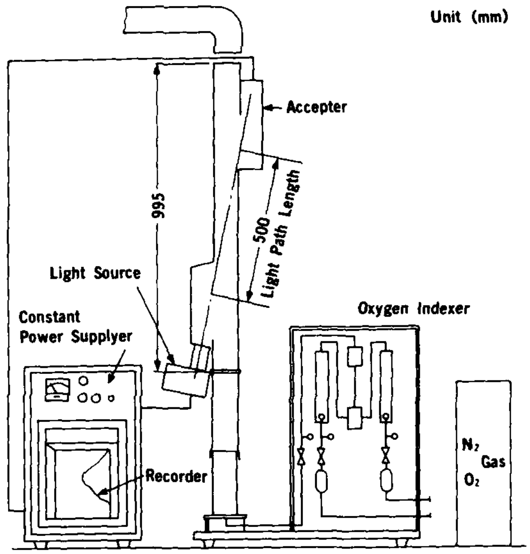


Fig. 2 Halogen Gas Sampler

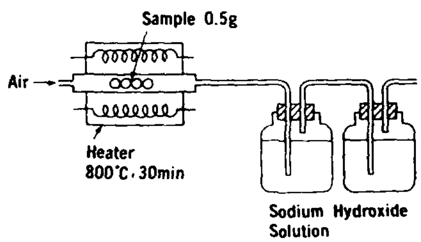


Table 3. Properties of Special EVA

(Crosslinked by Radiation)

Test	Units	Method	Typical Value
Tensile Strength, min.	kg/mm^2	JIS K6723	0.6
Elongation at Rupture, min.	%	JIS K6723	550
Air Oven Aging, 168hr at 150℃			
Tensile, min. Retention	%	JIS K6723	90
Elongation, min. Retention	%	JIS K6723	85
Oxygen Index, min.		JIS K7201	48
Brittleness Temperature	℃	JIS K6723	−20
Immersion in ASTM Oil No.2 4 days at 100℃		UL62	
Tensile, min. Retention	%		120
Elongation, min. Retention	%		105
Heat Distortion, 121℃, 2kg, max.	%	UL62	5
Volume Resistivity	Ω·cm	JIS K6760	1.1×10^{11}
Flammability		UL94	V-0

3. Trial Manufacture and Evaluation of Wires with Double-layer Insulation for Appliance Wiring

Special EVA is applicable only to particular low-voltage wires because of its low tensile strength and low dielectric strength - 1.1 x $10^{13}\Omega$.cm. Therefore, the possibility of making up for these deficiencies in mechanical strength and electrical properties with a separate polymer was investigated. The inevitable conclusion was that the application of a polymer blending technique would degrade the excellent flame retardant properties of Special EVA with no appreciable improvement in its electrical properties.

Thus, a double-layer insulation configuration employing a polymer with excellent mechanical and electrical properties around the conductor was investigated. As the inner layer insulation an ordinary LDPE with tensile strength of 2.3 kg/mm^2, elongation of 750% and M.I. 0.3 was adopted.

In the manufacture of this double-layer insulation wire, a double-layer fixed die originally developed by The Furukawa Electric Co., Ltd.[4] was employed and then crosslinked by an electron accelarator.

The construction of the trial manufacture sample is shown in Fig. 3, and the layout of the fixed die in Fig. 4.

Fig. 3 Construction of Test Samples

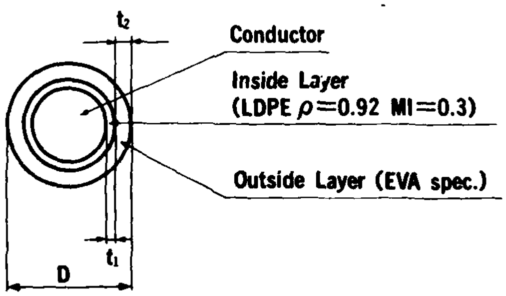
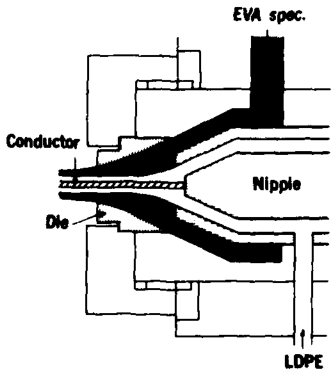


Fig. 4 Fixed Die for Double Layers Extrusion



3.1 Details of trial manufacture samples

By adopting three sizes of typical conductors commonly used as appliance wires, and varying the insulation thickness of the LDPE inner layer and special EVA outer layer, respectively, 25 kinds of wires were manufactured on a trial basis. Table 4 shows the construction of each sample.

Table 4 Test Sample Description

Sample No.	Conductor		Thickness of Inside Layer (t_1) mm	Thickness of Outside Layer (t_2) mm	Outer Diameter mm	Inside Layer Ratio ($t_1/(t_1+t_2)$)
	Type	Diameter mm				
1			0.	0.20		0
2			0.02	0.18		0.1
3			0.03	0.17		0.15
4			0.04	0.16		0.2
5			0.05	0.15		0.25
6	0.4ϕ Copper	0.4	0.07	0.13	0.80	0.35
7			0.09	0.11		0.45
8			0.10	0.10		0.5
9			0.13	0.07		0.65
10			0.15	0.05		0.75
11			0.17	0.03		0.85
12			0.10	0.40		0.2
13			0.15	0.35		0.3
14	20/0.18 Strand		0.20	0.30		0.4
15	0.5mm^2	1.0	0.25	0.25	2.0	0.5
16	Tinned Copper		0.30	0.20		0.6
17			0.35	0.15		0.7
18			0.40	0.10		0.8
19			0.10	0.50		0.17
20			0.15	0.45		0.25
21	37/0.26 Strand		0.20	0.40		0.33
22	2.0mm^2	1.8	0.25	0.35	3.0	0.42
23	Tinned Copper		0.30	0.30		0.5
24			0.35	0.25		0.58
25			0.40	0.20		0.67

3.2 Measurement Results

3.2.1 Elongation and tensile strength

Figure 5 shows a typical stress-strain curve. The tensile test of the insulation was conducted at a pulling speed of 500m/min on a gauge mark of 1 inch in accordance with UL 62.

Figures 6 and 7 show the elongation and tensile strength values, respectively.

The elongation of PVC or XLPE required by UL 62 is over 100%. However, since all samples show elongations of over 350%, all satisfy the standard.

The tensile strength requirement under UL 62 is more than 1500 psi (1.05kg/cm^2), so the inside layer ratio should be set to 0.25 or more.

3.2.2 UL 62 VW-1 flame test

In the UL 62 VW-1 flame test, with natural or propane gases as a gas source, a flame of a given length is applied to the wire such that the flame's blue core touches the wire 5 times for 15 sec each time. The testing device is shown in Fig. 8.

The judgment factors are:
1) The specimen should not flame longer than 60 sec after any application of flame. 2) No more than 25% of the kraft paper should be burned or charred. 3) The absorbent cotton should not be burned.

The test results for each wire are shown in Fig. 9, the 0.5mm^2 wire is most flammable, and

its inside layer ratio should be maintained at 0.3 or less.

3.2.3 Dielectric breakdown strength and insulation resistance

After a 1 hr immersion in water, all 30 m long wires were subjected to measurements of dielectric breakdown strength and insulation resistance. The results are shown in Figs. 10 and 11.

A dielectric breakdown strength at 3500V/min or more is sufficient for practical applications. This wire, with a breakdown strength of over 8,000V when the inside layer ratio is 0.1, is adequate for practical use.

The assured insulation resistance is 250MΩ•km or more for common PVC and 2500MΩ•km or more for FR-PE. The assured range of this double-layer insulated wire is 1000MΩ•km or more.

3.2.4 Optimal inside layer ratio

The worst wire in terms of flammability properties is $0.5mm^2$ conductor wire. If the inside layer ratio is raised above 0.4 for $0.5mm^2$ wire, the wire is disqualified for VW-1.

However, if the inside layer ratio is reduced to the extreme, the tensile strength will fall below $1.05kg/mm^2$. Consequently, a ratio somewhere around 0.3 is optimal.

Further, in the case of ϕ0.4 and $2.0mm^2$, an inside layer ratio as low as 0.5 is permissible. Of course, a larger inside layer ratio affords higher tensile strength and better electrical properties.

3.2.5 Typical properties of double-layer insulated appliance wires

A comparison was made between the major properties of the double-layer insulation and the PVC insulation UL style 1007. The results are shown in Table 5. The double-layer insulated wire is far superior in air-oven aging and oil-resistance properties and is adequate for use as the UL 105°C rating grade.

Table 5 Comparison of Properties with PVC Wire

Test			Halogen Free Flame Retardant Insulated Wire with Double Layers (Sample No 7)	UL1007 (None-Crosslinked PVC)	UL Value (105 C)
T S			1.15kg/mm²	1.75	1.05·
E L			580 %	250	100·
Air Over Aging	136 C × 7days	T S Retention	94 %	112.8	75·
		E L Retention	94 %	89.1	65·
	136 C × 14days	T S Retention	90.6 %	110.2	
		E L Retention	87.2 %	55	
	150 C × 7days	T S Retention	92.5 %		
		E L Retention	87.2 %		
Immersion in Oil ASTM No 2 100 C 96hr		T S Retention	94 %	123.3	80·
		E L Retention	109 %	68.8	80·
Heat Distortion (UL62) 120℃ × 300g			40 %	31.0	50·
Resistance to Soft Solder (MIL-W-16878/D)			Pass	Pass	
Heat Shock			Pass (150℃ × 1hr)	Pass (136℃ × 1hr)	
Cold Bend			Pass (−30℃)	Pass (−10℃)	

Fig. 5 Stress-Strain Curve of Insulation with Double Layers

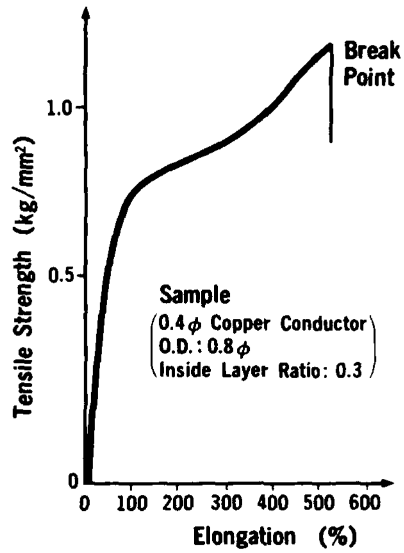


Fig. 6 Elongation of Insulation

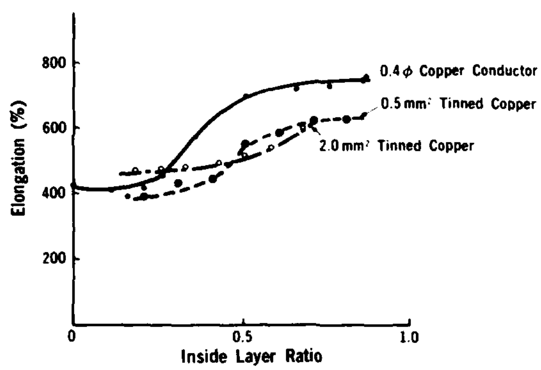


Fig. 7 Tensile Strength of Insulation

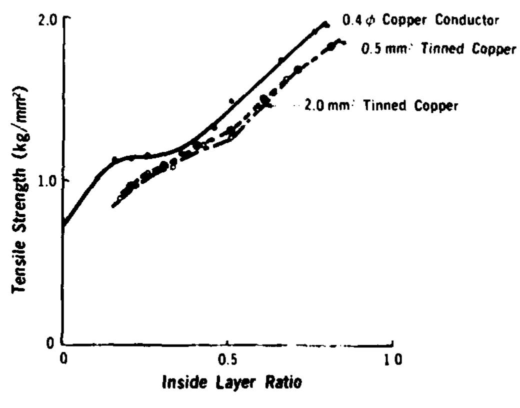
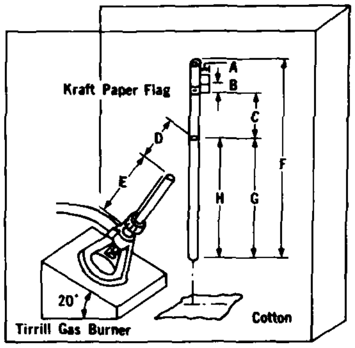


Fig. 8 Flame Test Device For UL62 VW-1



	mm
A	19.05
B	12.7
C	254.0
D	38.1

	mm
E	101.6
F	457.2
G	76.2
H	241.3

Fig. 9 Flammability of Wire

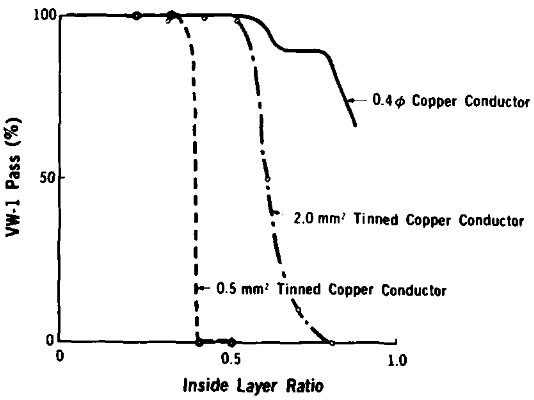
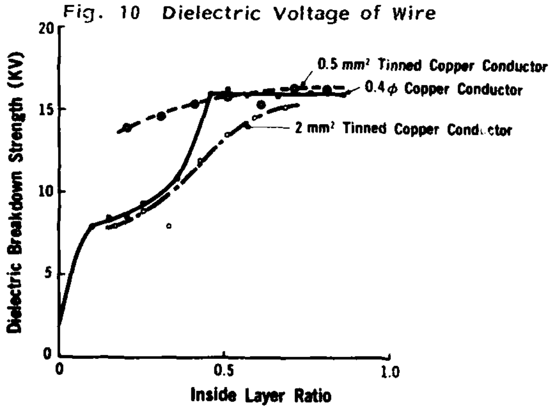


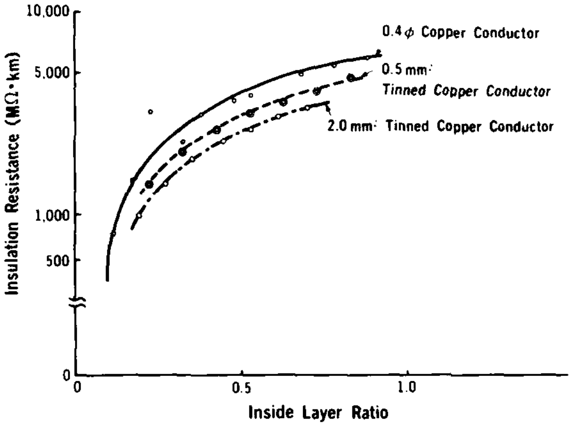
Fig. 10 Dielectric Voltage of Wire



4. Application to Wires for General Wiring

Unlike appliance wires, general wiring cables require water resistance as well as flame retardance satisfying the requirement for laying cables in vertical trays in IEEE 383. Furthermore cables used in nuclear power plants should clear the LOCA test. A test was made to determine whether halogen-free double-layer insulation can satisfy these requirements.

Fig. 11 Insulation Resistance of Wire



4.1 Sample

Assuming a 600V rating, the sample shown in Table 6 was manufactured on trial for evaluation.

4.2 Measurement Results

The measurement results are shown in Table 7. Since the LOCA test would take 100 days if it were conducted in exact conformity with IEEE 323, a short-term evaluation method based on IEEE 323 was employed.

The LOCA test conditions are shown in Fig. 12. The halogen-free double-layer insulated wires passed the IEEE 383 flame test as well as the water-resistance and LOCA tests which were considered difficult for XL-PVC or XL-FRPE wires to clear.

Table 6 Dimensions of Test Sample

Conductor	0 8φ
Inside Layer Ratio	0 35
Outer Diamater	2 4 [illegible]

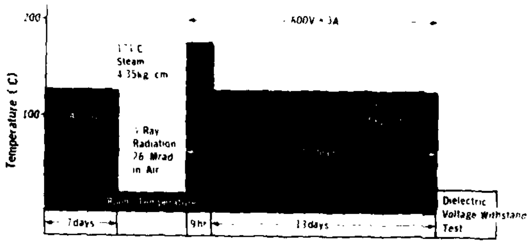
Table 7 Properties of Double-layer Insulated Wire

Test	Method	Units	Typical Value	Requirments of UL44 Class XL Thermosets
Tensile Strength	UL44	kg/mm²	1.05	1.05
Elongation	UL44	%	450	150
Capacitance & Stability Factor	UL44			
Specific Inductive Capacity after 24hr	UL44		4.8	6
Capacitance at 14days / Capacitance at 24hr	%		100	110
Capacitance at 14days / Capacitance at 7days	%		100	104
Stability Factor* at 14days			0.09	1
S.F* at 14days —SF at 24hr			0.283	0.5
IEEE383 Vertical Tray Flame Test	IEEE383		Pass	—
LOCA-Test	Based on IEEE323**		Pass	—

*S.F. [illegible] between the percentage power factors measured with [illegible]

** Conditions are shown in Fig. 12.

Fig. 12 LOCA Test Conditions



5. Conclusion

A crosslinked halogen-free, double-layer insulated wire that supersedes PVC, XL-PVC, and XL-FRPE insulated wires for appliance wiring was developed. This wire has non-corrosive properties and high flame retardance satisfying UL 62, VW-1. Furthermore, the halogen-free, double-layer insulated wire for general wiring has passed all the water resistance test under UL 44, the vertical-tray flame test under IEEE 383 and the LOCA test based on IEEE 323. The newly developed halogen-free, double-layer insulation is applicable to appliance wires for continuous use over 40,000 hours at 110°C, control and power cables for general use such as buildings, subways, and ships, and cables and wires for nuclear power plants. In addition to the inherent halogen-free composition, surprisingly the observed CO generation was one-fifth that of natural polyethylene and no black smoke was produced in combustion.

References

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2) H. Harbort, 29th IWCS Proceedings 263 (1980)
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4) K. Fuse, 27th IWCS Proceedings 62 (1978)

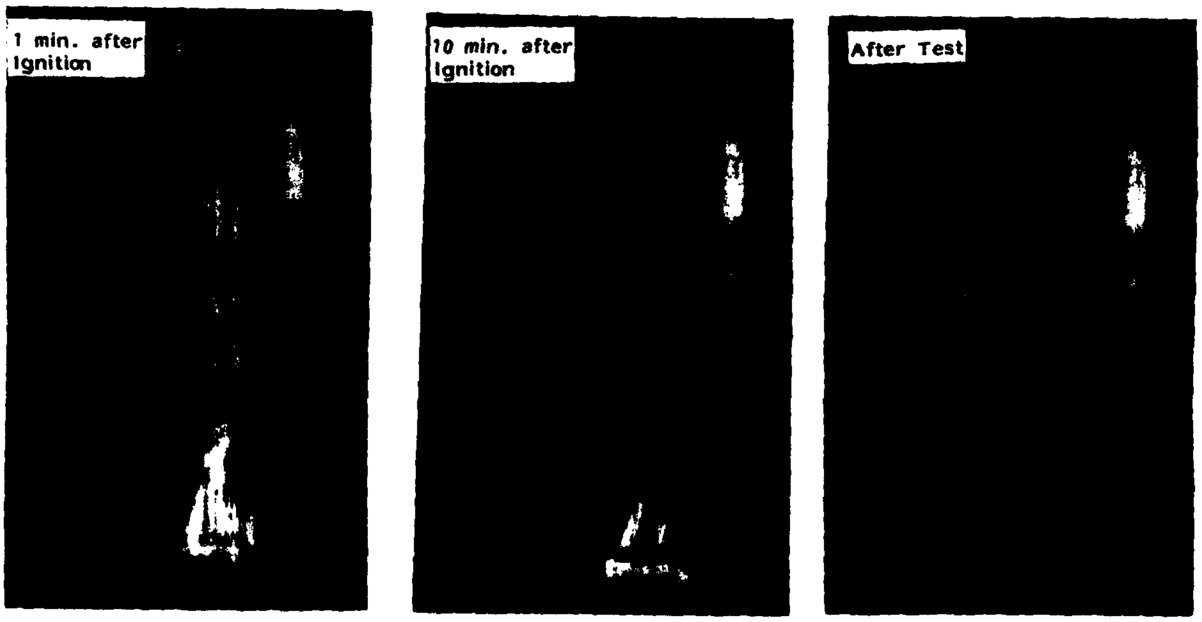
Photo 1 Cross Section of Halogen-Free Flame Retardant Insulated Wire

Conductor: 2.0 mm²
O.D.: 3.0 mm
Inside Layer Ratio: 0.42

Photo 2 IEEE 383 Flame Test

Sample: Halogen-Free Insulated Wire

Conductor: 0.8ø
O.D.: 2.4 mm
Inside Layer Ratio: 0.35



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